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Preparation of silicalite-1 layers on Pt-coated carbon materials: a possible electrochemical approach towards membrane reactors

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Abstract

A novel kind of composites is synthesized due to the outstanding properties of carbon materials. Metallic platinum is deposited on porous carbon discs by means of Potential Step Deposition (PSD) under potentiostatic conditions. Afterwards, the Pt-coated discs were covered completely with colloidal zeolite (silicalite-1) crystals by means of the novel Electro Phoretic Deposition (EPD) methodology. After standard hydrothermal treatment, the seed crystal coating becomes continuous, crack-free and well-intergrown, giving rise to a layer of silicalite-1 crystals of different sizes. It must be noted that Pt combined with the secondary growth methodology has a extremely important effect on the orientation of the growing zeolite crystals. These novel materials have a wide range of potential applications as membrane reactors and/or catalyst membranes after activation (i.e. template removal by calcination) of the zeolite crystals.

Keywords: Silicalite-1; Electro phoretic deposition; Membrane reactors; Carbon materials

1. Introduction

As a direct consequence of the many applications of crystalline zeolites, such as ion exchangers, adsorbents, and molecular sieves [1], and all the possibilities implied therein, increasing attention has been paid to preparing zeolite membranes over the years [2].

Considering the many different strategies that have been employed nowadays [3–7] and the wide variety of supports that have been tested already [3–24], one might think that the issue of preparing a supported zeolite membrane has been successfully achieved. This, however is not so, because even from the initial approach of the direct treatment of the support with a zeolite precursor solution [8], it was clear that a significant layer thickness was needed to obtain a continuous film [25]. More recently, the seed film method has been introduced with the aim to better control the growth of zeolites on the studied supports [26–33]. This methodology can be adapted to substrates with rather different chemical nature, making the synthesis of thin oriented layers of zeolite crystals possible (see for example Refs. [26,31]). The main aim of the seed film method, attempted by some different approaches, is to systematically cover the surface of the support with a layer of zeolite crystals so that, according to the classical theory of crystal formation, the nucleation step is thus skipped. The advantages brought for by this method are that shorter synthesis times are needed for a continuous zeolite layer to grow on the support and that preferential orientation is more easily achieved.

On the other hand, quite recent studies [34,35] have tackled the issue of membrane reactors, studying the applicability of such aforementioned zeolite membranes

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to continuous membrane reactors (CMRs) [34] or as selectivity enhancers for reactive gas sensors [35]. In the latter case, the addition of a zeolite membrane improves the selectivity of semiconductor-based sensors. Although finally applied to a system that could be named a membrane reactor, the zeolite membrane itself is only used as a molecular sieve layer, in what is known as an inert membrane reactor. Up to now, some works [36,37] have reported the use of a zeolite membrane coupled with a catalytically active species in intimate contact but outside the membrane, thus constituting a so-called combined membrane reactor. This work adds up to these aforementioned works, in which a separation layer is deposited on a metallic catalytically active layer. Other examples of membrane reactors can be found in the literature (see for example, Refs. [38,39]), but in such cases, the separation layer (zeolite) acts as the catalyst itself (catalytic membrane reactor), and thus are different from those presented in this communication, a combined membrane reactor, in which the catalytic material can be inside or outside the separation layer, but not being a part of it.

Recent reports have shown the interesting applications of Electro Phoretic Deposition (EPD) [40,41] as a simple suitable method to deposit homogeneous films of colloidal zeolite seeds on materials with different shapes, although to the best of our knowledge, there have been few results on the preparation of zeolite membranes using EPD [41]. Our research group has very recently reported the successful synthesis of continuous, defect-free layers of silicalite-1 on carbon materials by secondary growth using EPD as the seeding technique [42].

In conclusion, the purpose of the present work is to integrate both the molecular sieving layer and the catalytic layer onto the same system, thus making a combined membrane reactor. The scope for doing this is mainly focused on the electric properties of carbon (that is, being carbon electricity conducting). From this point of view, our two main objectives would be to first deposit a catalytically active species (metallic platinum) on the surface of a carbon support by means of the Potential Step Deposition (PSD) method under potentiostatic conditions and then perform the EPD of a coating of zeolite colloidal seeds in order to grow continuous zeolite films on top of the catalytically active species by standard hydrothermal treatment. The remarkable influence of the deposition of platinum on the final composite is discussed.

2. Experimental

2.1. Preparation of the supports and platinum deposition

Macroporous carbon discs were cut from a macroporous carbon sheet (thickness = 0.5 mm, mean pore size 0.7 μm) provided by Poco Graphite (DFP-1). For the electrochemical deposition of Pt under potentiostatic conditions (constant potential), an electrochemical cell of three electrodes was used (see Fig. 1). All the experiments were performed in a 5×10^{-3} M H_2PtCl_6 + 0.5 M H_2SO_4 (Merck, suprapur) solution using a EG&G Potentiostat/Galvanostat model 263A. The counter electrode was a platinum wire and the reference electrode was a reversible hydrogen electrode (RHE) immersed in a 0.5 M H_2SO_4 solution in water. All solutions were prepared with high-purity water (Purelab ultra Elga system). The macroporous carbon discs acted as the working electrode. The current densities were calculated using a value of geometric area of 0.57 cm^2, which was exposed to the solution. In all cases, the initial potential corresponds to a value in which no platinum deposition is produced (0.8 V vs. RHE)

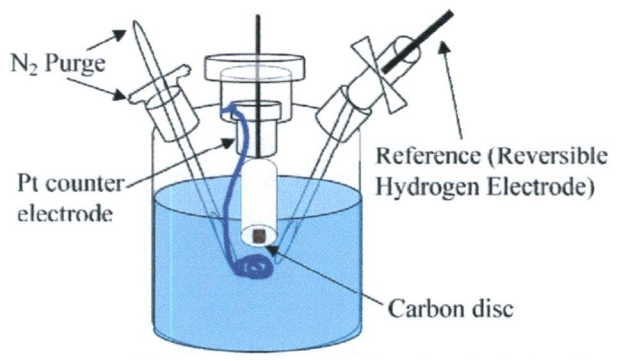

Fig. 1. Image and flow diagram of the electrolytic cell used for the deposition of Pt^0 on the carbon discs.

2.2. Seeding of the supports

A suspension of silicalite-1 crystals with particle size ~100–200 nm was prepared according to the method reported by Person et al. [43] by hydrothermal synthesis of a clear solution at 333 K for two weeks with the following composition:

$$1SiO_2 \cdot 4EtOH \cdot 1TPA\text{-}OH \cdot 49H_2O$$

This silicalite-1 suspension was used with the non-oxidized carbon discs, which were seeded using the setup depicted in Fig. 2. Constant current density was applied referred to the geometric area of the carbon disc that acts as a cathode, using a Pt counter-electrode [40]. A controlled current is applied to the circuit under static conditions. The area of the graphite disc (0.57 cm^2) that is exposed to the seeding suspension is controlled by means of a Teflon device. Both the current intensity and voltage of the circuit are monitored through the whole process.

2.3. Zeolite crystal growth and compact layer formation

After electroseeding, the silicalite-1 layers were prepared at various temperatures for different times for

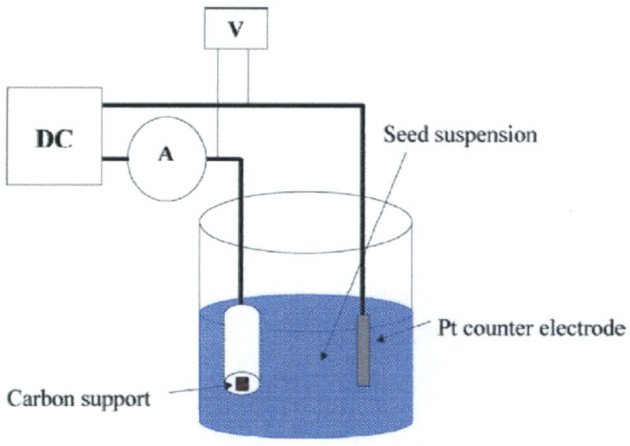

Fig. 2. Image and flow diagram of the setup used for the EPD of seed crystals on the carbon support.

comparison purposes. Silicalite-1 layers were grown on the carbon supports by standard hydrothermal synthesis as described in Refs. [7,21,33,42]. The silicate solutions were obtained from TEOS (tetraethyl orthosilicate) (ALDRICH 13,190-3), adding high-purity NaOH (when necessary) (ALDRICH 30,657-6). Tetrapropylammonium hydroxide (TPA-OH) (ALDRICH 25,453-3) and tetrapropylammonium bromide (TPA-Br) (ALDRICH 2556-8), were used as the templating agents. A typical composition of the synthesis solutions was:

$$1SiO_2 \cdot 0.30TPA\text{-}OH \cdot 0.15NaOH \cdot 14.98H_2O \quad (1)$$

All synthesis were performed by triplicate to check the reproducibility of the experiments.

2.4. Characterisation of the materials

The crystalline phases synthesized were characterized by X-ray powder diffraction using a SEIFERT 2002 equipment. CuKα (1.54 Å) radiation was used. The scanning velocity was 2°/min, and the 2θ range scanned was from 2° to 60°.

The morphology of the synthesized composites was studied by Scanning Electron Microscopy (SEM) using a Hitachi S-3000N equipment. The chemical composition of the samples was analyzed by EDX (coupled to the SEM equipment, Link QX-200).

3. Results and discussion

3.1. Platinum deposition by PSD

As a first approach towards the deposition of metallic platinum on the carbon supports, we conducted two sets of experiments: (i) keeping a fixed voltage pulse (fixed initial and end pulse voltage) and applying the corresponding pulse for different times. Fig. 3A and B show

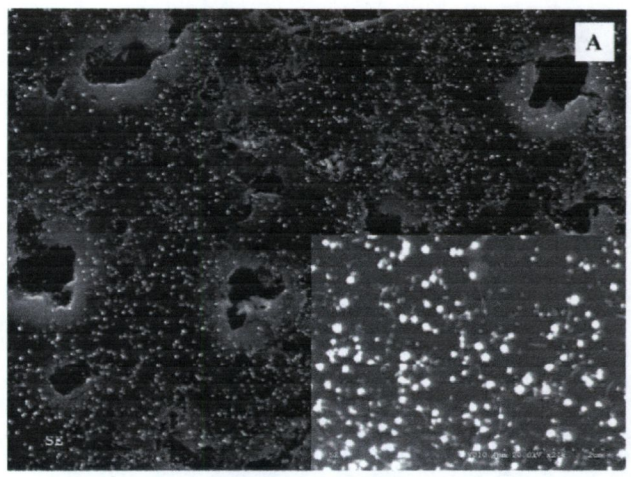

Fig. 3. SEM images of the carbon supports after PSD with an initial pulse voltage of 0.80 V and an end pulse voltage of 0.05 V for (A) 15 s and (B) 60 s.

the results corresponding to such experiments. It is clear from the SEM images that longer PSD times yield a better coverage of the carbon supports with metallic nuclei and a larger particle size. In this sense, not only did we intend to obtain a coverage as good as possible, but also a reasonably small particle size, in order to maximize the dispersion of the metal atoms. For this reason, we conducted the second series of experiments; (ii) keeping the initial pulse voltage at 0.8 V, the end pulse voltage was changed from 0.05 to 0.15 V and applying the corresponding pulse for 15 s. Figs. 3A, 4A and B show the carbon supports after undergoing PSD under such conditions. The following can be seen from the figures: As we increase the end pulse voltage, the average particle size decreases from approximately 200 nm to approx. 40–50 nm. From Figs. 3A and 4A it seems that a change in the end step voltage from 0.05 to 0.10 V only contributes to the amount of Pt^0 nuclei present on the carbon surface, whereas a further increase of 0.05 V up to

0.15 V (Fig. 4B) provokes the support to be covered with substantially smaller metallic particles.

Another extremely important issue to address at this point is to analyze the evolution of the delivered charge with time, which can not only give us an idea of the amount of platinum deposited on the carbon surface through very simple calculations, but also the mechanism through which the deposition of metallic particles is taking place [44]. When the electrochemical nucleation and growth of different species takes place, according to the model described by Scharifker and Hills [45], there can be two possible nucleation mechanisms according to their theoretical relationship, instantaneous nucleation or progressive nucleation. In the former mechanism, all the nuclei are rapidly created and their numbers remain constant during the growth process. The other possible mechanism is the progressive nucleation where the actual nucleation rate is low and new nuclei are continuously forming during the whole deposition process. The work of Bade et al. [46] is a very good example of how to apply the corresponding equations to the progressive and instantaneous nucleation mechanisms.

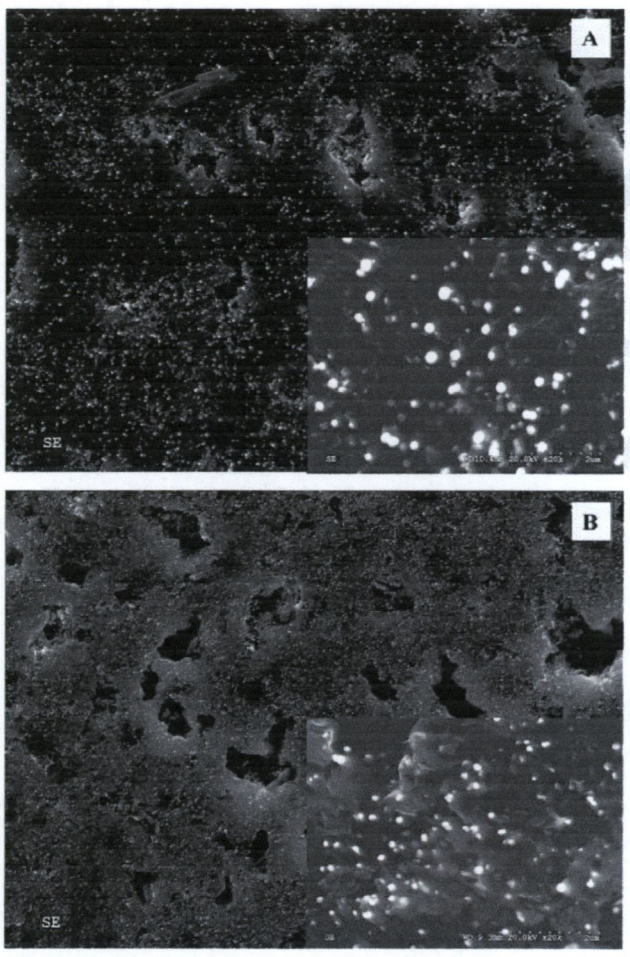

Fig. 4. SEM images of the carbon supports after PSD for 15 s with an initial pulse voltage of 0.80 V and a end pulse voltage of (A) 0.10 V and (B) 0.15 V

Thus, Fig. 5 shows the current vs. time graphs for Fig. 3A. Nevertheless, it must be noted that the results apply to all other figures corresponding to deposited Pt^0 on the carbon supports. It is obvious that the data fit those corresponding to the *progressive nucleation* model almost perfectly, which is in agreement with our experimental observations (the fairly broad metallic particle size distribution observed by SEM suggested that new nuclei were being formed continuously throughout the PSD process).

3.2. Seeding of the Pt-coated supports

As already mentioned in the introduction section, our research group has already reported the preparation of continuous layers of silicalite-1 on carbon discs by electrochemical methods [42]. In the aforementioned communication we analyzed the influence of time and applied current density of EPD in the seed crystal deposit on the surface of our carbon support, reaching the conclusion that after an EPD process at 9 mA/cm^2 during 30 min, the seed crystal layer deposited on the carbon support is deemed appropriate for crystal growth. Thus, all the forthcoming seeded materials mentioned in this paper underwent the same EPD conditions (current density: 9 mA/cm^2 EPD time: 30 min). Fig. 6 shows a top-view of one of such seeded materials. It is obvious from the image that a complete coverage has been achieved, and from our previous results we have concluded that it is suitable for the growth of continuous zeolite films by standard hydrothermal treatment. It must be noted that the deposition of metallic platinum does not hinder the use of the resulting carbon discs as electrodes for electrophoresis. In fact, the results obtained for both the Pt-coated and non-coated carbon supports proved to be equally satisfactory.

3.3. Zeolite growth on the seeded, Pt-coated supports

Although the seed crystals layer might seem continuous from the top-view SEM image, the space between two crystals (i.e. intercrystalline gaps) is very significant, so that in the whole surface of the carbon disc, there is a considerable space that is *not* covered by zeolite crystals and that is thus not affected by the molecular sieving properties of zeolites. This, as a matter of fact, is the main focus of our interest since we intend to use the resulting materials as membranes in the near future. As a result, the sealing off of the intercrystalline space is mandatory towards possible membrane applications. As mentioned in the Experimental section, the zeolite growth took place by immersion of the seeded, Pt-coated supports in the synthesis solution in a Teflon-

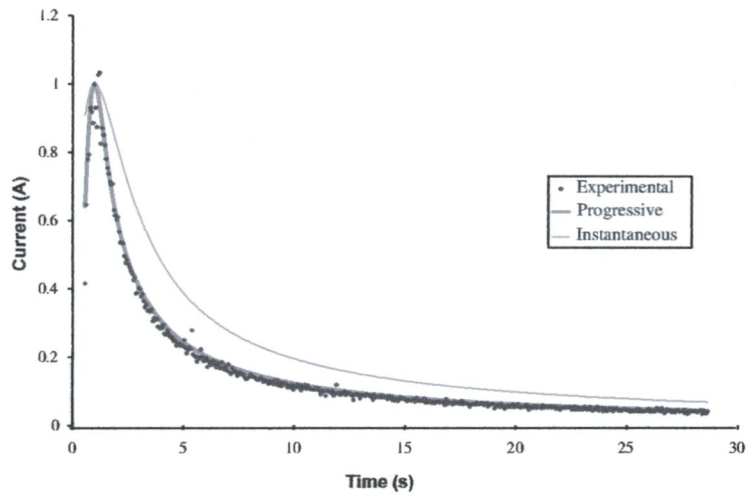

Fig. 5. Current vs. Time plot for the material shown in Fig. 3A.

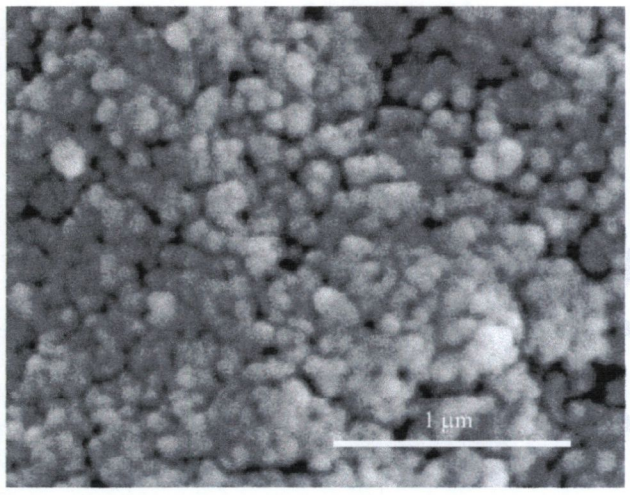

Fig. 6. SEM image of a carbon disc after 30 min of EPD at 9 mA/cm^2.

lined autoclave by means of standard hydrothermal treatment. The composition and the temperatures of the synthesis that were carried out are:

$$1SiO_2 \cdot 4EtOH \cdot 0.15TPA\text{-}OH \cdot 0.15TPA\text{-}Br139.46H_2O$$
for 72 h at 458 K and 433 K (2)

$$1SiO_2 \cdot 4EtOH \cdot 0.30TPA\text{-}OH \cdot 0.15NaOH \cdot 14.98H_2O$$
for 72 h at 458 K and 433 K (3)

$$1SiO_2 \cdot 4EtOH0.047TPA\text{-}Br \cdot 0.278NaOH \cdot 41.72H_2O$$
for 72 h at 458 K and 433 K (4)

$$1SiO_2 \cdot 4EtOH \cdot 0.11TPA\text{-}OH \cdot 40.39H_2O$$
for 72 h at 458 K and 433 K (5)

Fig. 7A and B present the SEM images of the top-view of the composites obtained after hydrothermal treatment for 72 h using synthesis solution composition (2). Although the images are not shown, the composites obtained for compositions (3) and (4) yielded carbon discs covered with a continuous, compact zeolite layer (the results corresponding to synthesis composition (5) will be discussed in the next section). In the case of syntheses (2)–(4), the experiments yielded continuous layers of silicalite-1 on the carbon supports with crystals sizes ranging from 1 to 5 μm with random orientation. In this respect, SEM pictures corresponding to only composites obtained from synthesis (2) are presented, since they are representative of the composites obtained using the aforementioned syntheses conditions. After hydrothermal treatment and sonication, all membranes were mounted in a permeation cell and they were tested for N_2 permeation, showing no gas flow through the membrane, thus indicating the good quality of the resulting zeolite layer.

3.4. Influence of the platinum deposit on the orientation of the zeolite crystals

In the previous section, the data corresponding to the growth of silicalite-1 of the seeded, Pt-coated supports for synthesis composition (5) were purposely overlooked. The reason for this to happen is that there was an extraordinary feature concerning the fashion with which the zeolite crystals grew in that particular case. Fig. 8A and B show the SEM images corresponding to the top-view of the obtained composites. It is noticeable that the crystals in the two samples have a strong preferential orientation. This can further be corroborated by checking the X-ray Diffractograms (Fig. 9) showing peaks corresponding to the $(0kl)$ (in the case of Fig.

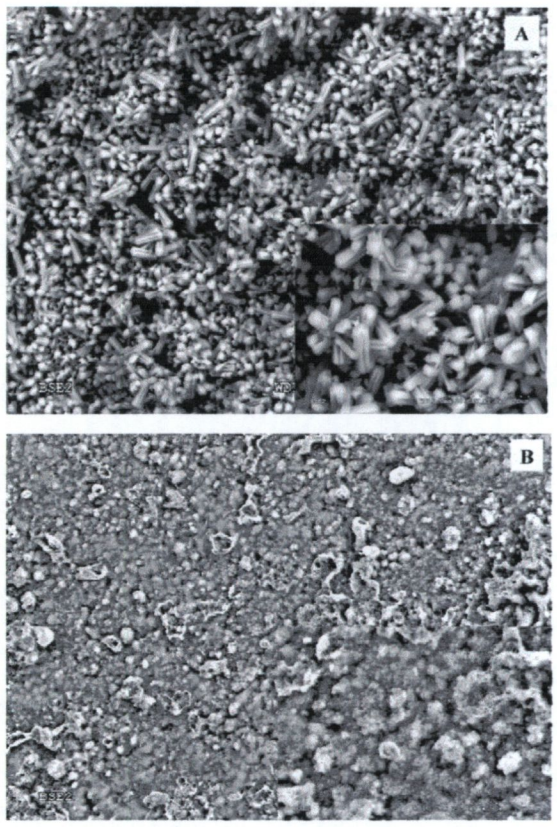

Fig. 7. SEM micrographs of the composites prepared from the Pt-coated, seeded supports, after hydrothermal treatment using the synthesis conditions specified in section 3.3. Note: The images correspond to synthesis composition (2) at (A) 458 K and (B) 433 K.

8A), and (0 k 0) and (1 0 3) (in the case of Fig. 8B) reflections that are noticeably more intense than those found in the polycrystalline X-ray Diffractogram for silicalite-1 [47], thus further corroborating the preferential orientation (see Fig. 9).

After ascertaining the reproducibility of the remarkable results obtained (the synthesis was repeated on three different seeded, Pt-coated supports, obtaining identical results to those discussed above) and in order to further investigate the subject, the same synthesis procedure (synthesis solution composition, hydrothermal treatment time and temperature) was repeated using a carbon disc (without any seeding or Pt deposition), a seeded carbon disc, and a Pt-coated disc without any seeding. In all three cases (the results corresponding to the experiments related to the seeded disc can be found in a previous communication by Berenguer-Murcia et al. [42]), no preferential orientation occurs. The results from all these experiments seem to suggest that *only* when a seeded, Pt-coated carbon disc is used as a support, the final zeolite layer has a noticeable preferential orientation. Fig. 8C and D show the SEM images of silicalite-1 grown on the unseeded and seeded carbon disc (both non-Pt coated) and, as it can be seen, there is no preferential orientation whatsoever for the grown crystals (this can be better acknowledged from the insets in each figure and from Fig. 9 where the corresponding diffractograms can be found). It is thus remarkable that the deposition of Pt has such an effect concerning the growth of crystals on its surface. As Ref. [19] summarizes: "The final attachment to the support is obviously strongly dependent on the type of support. Crystals can chemically bind to the surface if surface OH groups are present". Thus, considering that the Pt particles have a high density of surface OH groups, the interaction between the metallic particles and the zeolite crystals must be significant. Additionally, the potential applied changes the surface charge of the Pt particles which can favour the interaction of the seed crystals.

The difference in orientation for the samples prepared at 458 and 433 K can be explained on the basis of crystal growth kinetics provided that the support is sufficiently hydrophilic. At 458 K, the crystals grow at a much faster rate, and thus the fastest-growing crystal direction (the c direction) is oriented towards the SiO_2-rich part of the reaction system (which would be the synthesis solution). At 433 K, though, this crystal growth rate is noticeably inferior and thus, considering the alkali-free environment, the crystal growth mechanism is most probably that described by Jansen et al. [19]. It might seem highly unlikely that with an uneven and hydrophobic as surface as that of our carbon support it would be possible to achieve such crystal orientation. In spite of the extreme surface roughness of our support, the metallic platinum particles may act as extremely efficient anchoring locations, playing a remarkable role in terms of both crystal growth and orientation. In fact, given the fairly homogeneous coating of Pt particles on the surface of the support, we may be introducing a "metal-like" surface that is extremely convenient. The introduction of these particles with a high density of surface OH groups enhances the crystallization kinetics. Furthermore, it is a well-known fact that the secondary growth method improves the kinetics of zeolite layer formation.

The combination of these two effects (Pt particles and seeding) provokes our support to behave as a "classical" hydrophilic support, thus the remarkable results. It may then seem that the presence of the small Pt particles favours a strong attachment of the silicalite-1 colloidal seeds which will not redistribute significantly during the hydrothermal treatment, making it thus possible to grow oriented zeolite films. However, and as it can be seen from Fig. 8B, the roughness of the carbon discs prevails sometimes causing poor crystal orientation in some regions. Then again, it must be highlighted that the deposition of Pt on the surface is a critical factor for the crystals to grow with their b direction perpendicular to the support surface, which is something we have never come across using carbon discs as supports.

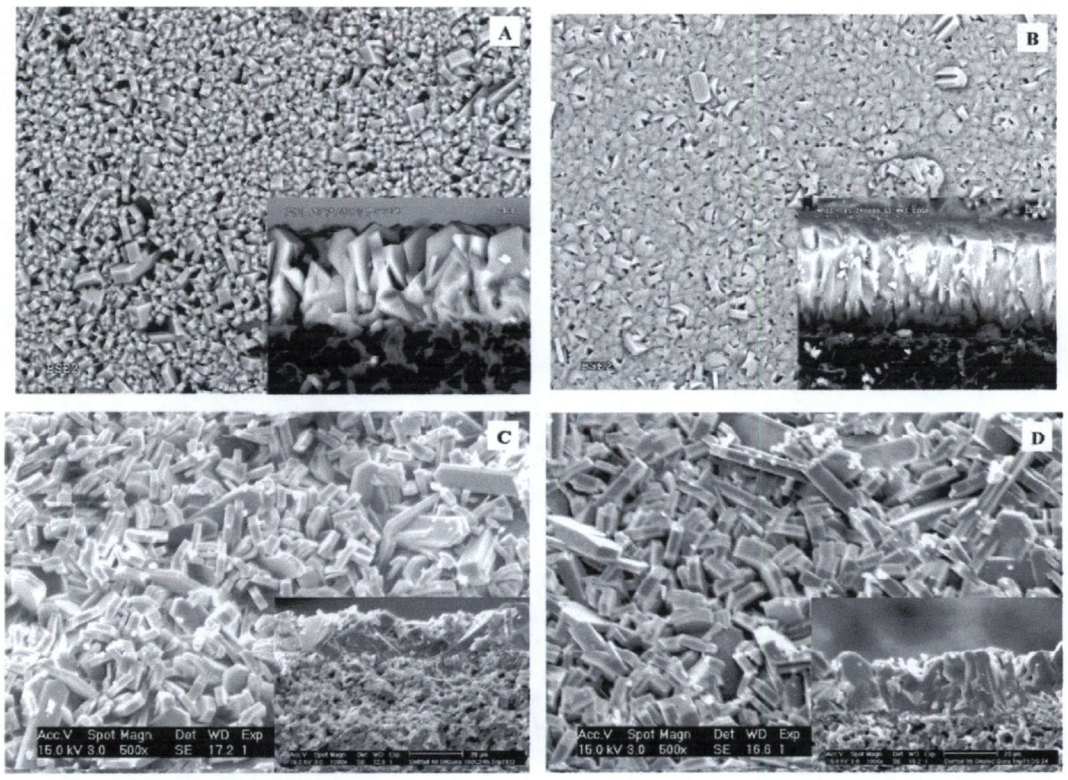

Fig. 8. SEM micrographs of the composites prepared from the Pt-coated, seeded supports, after hydrothermal treatment using the synthesis solution composition (5) at (A) 458 K and (B) 433 K. Figures (C) and (D) correspond to the same synthesis performed on the unseeded, *non* Pt-coated support and on the seeded, non-Pt coated support, respectively.

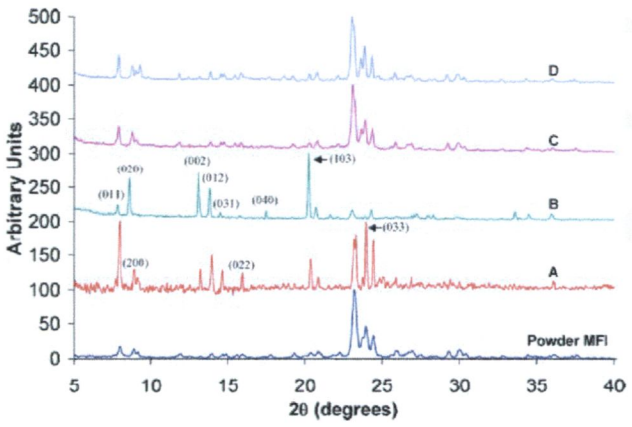

Fig. 9. X-ray Diffractograms for the composites shown in Fig. 8A–D. The X-ray Diffractogram for the powder form of MFI crystals is also shown for comparison purposes.

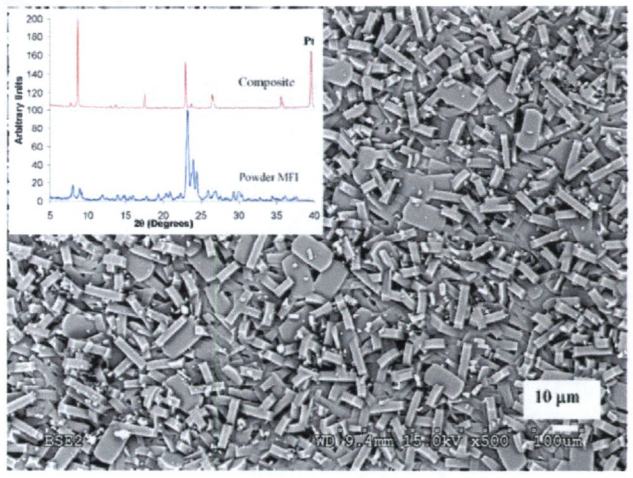

Fig. 10. SEM micrographs of the composites prepared following synthesis (4) after hydrothermal treatment at 433 K using a Pt disc as a support. Inset: XRD patterns for the composite and the MFI powder.

On the other hand, and to deepen the matter, we performed synthesis (5) at 433 K on a (i.e. highly smooth surface and non-porous) bulk Pt disc. Fig. 10 shows a SEM picture of the obtained composite, and the inset in the same figure shows how the peaks corresponding to the $(0k0)$ reflections are much more intense than those found for the composite obtained using the same synthetic pathway using a seeded, Pt-coated carbon disc, thus supporting our hypothesis of the latter mentioned support showing a behavior similar to a hydrophilic support like Pt (the Pt disc presented a water contact angle inferior to 30°, showing a noticeable hydrophilic character).

4. Conclusions

In summary, composites comprising a molecular sieve layer, a catalytically active section and a macroporous support have been synthesized by a simple and straightforward method thanks to the remarkable electrical properties of the carbon support used. Its conductivity has enabled the deposition of both metallic particles by PSD (which may act as a supported catalyst) and colloidal zeolite crystals by EPD, which are used in the following step as seeding nuclei. The coating of zeolite seeds is transformed into a continuous layer of well-intergrown silicalite-1 crystals by standard hydrothermal treatment. It is very important to highlight the significant changes that the addition of metallic Pt in the system brings forth: the presence of small metallic particles during secondary zeolite growth makes the growing zeolite crystals to have a certain orientation that can be selected by careful control of the hydrothermal synthesis. The influence of the metallic deposit coupled to the enhancement in crystallization kinetics dramatically changes the behavior of the support when submitted to hydrothermal treatment. Further work needs to be done in order to prove these materials as membrane reactors, but the possibilities and implications brought forth by the synthesis presented in this paper make these entirely novel composites promising Continuous Membrane Reactors (CMRs).

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